



Natural gas removal of hydrogen sulphide and mercaptans

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ARTICLE INFO

Article history:

Received 11 October 2010

Received in revised form

14 November 2011

Accepted 15 November 2011

Available online 23 November 2011

Keywords:

Natural gas

Hydrogen

Sulphide

Mercaptans

ABSTRACT

Methane is the main component of natural gas but not the only one. In fact in natural gas are usually present also higher alkanes (ethane, propane, butane, and pentanes), water, nitrogen carbon dioxide and sulphur containing molecules.

Within sulphur containing molecules the most abundant is hydrogen sulphide, but mercaptans, elemental sulphur and, less frequently, carbonyl sulphide may also be present.

The treatment of natural gas in order to remove sulphur containing compounds is dependent not only on the quantity of these compounds but also on the volume of natural gas to be treated.

In this review, will be illustrated the main industrial processes to remove H_2S , in large (more than 20 ton sulphur/day), intermediate (20 kg sulphur/day < quantity < 20 ton sulphur/day) and small amounts (lower than 20 kg sulphur/day). Mercaptans removal methods according to their molecular weight and content will be discussed.

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1. Introduction

The content of impurities in pipeline gas is very low and even lower in gas fed to LNG plant while the gas coming from wells may contain contaminants each one in quantity higher than 10%.

Natural gas coming from the well is first compressed in order to remove the oil and condensate then treated in order to remove CO_2 and H_2S .

The methods for separation of CO_2 and/or H_2S depend on their quantity. For large quantities the preferred method consists of absorption in aqueous solution, whose active component depends on natural gas composition. In fact, if both H_2S and CO_2 are present, amine solution (MEA, DEA, MDEA, etc.) are currently used and the choice of the amine is related to the CO_2/H_2S ratio present in the mixture [1]. These processes are very energy consuming since a chemical reaction takes place between the acid component and the amine. If only CO_2 is present amines may be used as well as a treatment with alkali salt solutions. For removal of bulk quantities of CO_2 and H_2S are currently used also physical solvents, in which acid components are adsorbed without reaction: the most diffused are Selexol [2] and Rectisol [2]. The proper choice between chemical and physical solvents depends on evaluation of different features as described in Table 1.

Other methods for CO_2/H_2S bulk removal, which are currently being developing, are based on PSA and membranes. If the quantities of CO_2 and/or H_2S are low (less than 25 kg equivalent

sulphur/day) other methods could preferably be applied such as PSA, membranes or, scavengers [3].

H_2S and other sulphur containing molecules after the separation can not be disposed as such in the atmosphere, but conversion processes have to be applied in order to convert them to elemental sulphur or other inorganic, non toxic, compounds.

2. H_2S removal

As previously mentioned the methods for the disposal of H_2S from natural gas may be divided in three main groups: methods for the removal of large quantities of H_2S , i.e. more than 20 equivalent ton of sulphur/day, intermediate scale, quantities of equivalent sulphur between 20 ton of sulphur/day and 25 kg equivalent ton of sulphur/day, and small scale for quantities of equivalent sulphur lower than 25 kg/day (Figs. 1–3).

2.1. Process for removal of H_2S (large quantities)

There is one industrial process for the disposal of large quantities of H_2S : Claus process [4].

The chemical path of Claus process is quite simple: about 1/3 of H_2S to be treated is burnt in a flame with sub-stoichiometric quantity of air to transform it to sulphur dioxide according to: $2H_2S + O_2 = SO_2 + 2H_2O$ [4]. This reaction is very exothermic ($\Delta H^\circ = -519 \text{ kJ/mol}$) and heat of reaction is removed through heat exchangers. The second reaction consists of conversion of SO_2 produced with unreacted H_2S according to: $SO_2 + 2H_2S = 3/8S_8 + 2H_2O$. Sulphur is obtained as final product of high quality (sulphur purity >99.9%) and it is commercialized without further purification.

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Table 1
Comparison between chemical and physical solvents.

Chemical solvents	Physical solvents
Relatively insensitive to H ₂ S and CO ₂ partial pressure	Very sensitive to H ₂ S and CO ₂ partial pressure
Can reduce H ₂ S and CO ₂ to ppm level	May be difficult to meet H ₂ S specification
High energy requirement for regeneration	Low energy requirement for regeneration
Not selective between H ₂ S and CO ₂	Can be selective between H ₂ S and CO ₂
Treated gas leaves saturated with water	Treated gas leaves dry

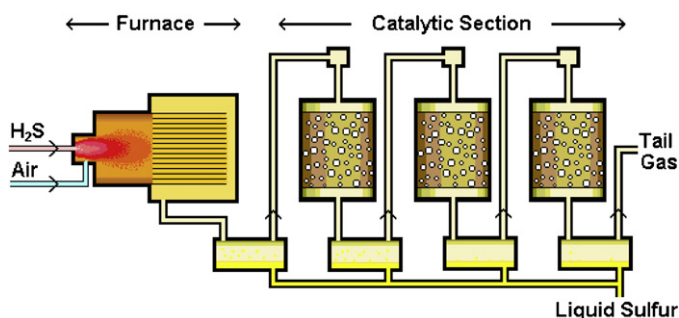


Fig. 1. Simplified scheme of Claus process.

While the first step of Claus process is simply a combustion, the second one is catalytic and the catalysts mainly used are based on activated alumina or titania.

Claus process may be performed in two different configurations: straight-through and split-flow [4]. Straight-through configuration is used for concentrated H₂S streams (H₂S concentration $\geq 40\%$). In this configuration all acid gas is passed through the reaction furnace and waste heat exchanger. A significant amount of sulphur is produced and condensed before the gas enters the first catalytic bed.

If the concentration of H₂S is not high enough the temperature of the flame is not too low to decomposed ammonia and carbon dioxide present in the feed therefore elemental carbon is formed and sulphur is not commercial grade (carsul formation).

In split-flow configuration 2/3 of the gas stream is fed directly to the catalytic reactor while 1/3 is fed to the burner. In this configuration usually no production of sulphur takes place in the burner.

This configuration can treat H₂S streams whose concentration is between 20% and 40%.

However using both configurations H₂S is far to be completed and a tail gas treatment section is needed. The stream from the

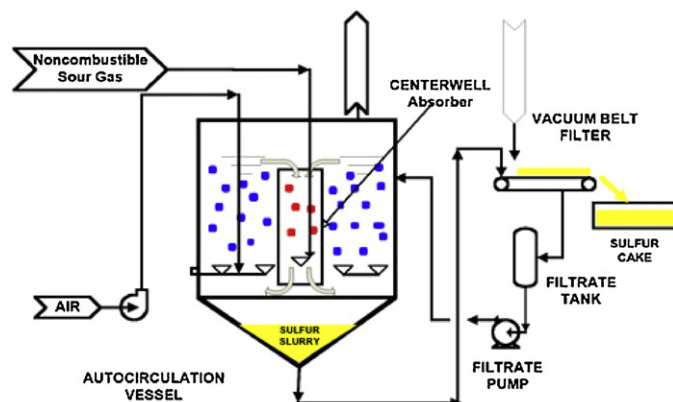


Fig. 2. LOCAT® autorecirculation scheme.



Fig. 3. Eni pilot plant.

last Claus reactor containing different sulphur compounds (H₂S, SO₂, COS, CS₂ and elemental sulphur) is completely hydrogenated and H₂S recycled to the first reactor. SCOT (Shell Claus off-gas treating) [5] is the most common tail gas treatment unit of Claus process. Scott uses typical hydro treating catalysts such as cobalt-molybdenum or nickel-molybdenum at temperature about 300 °C. Reducing gas is constituted of a mixture of CO and H₂, produced by sub-stoichiometric combustion of fuel.

Another improvement to the Claus process is the Superclaus process [6]. The Superclaus process offers an overall sulphur recovery of up to 99.5% without any tail gas treatment, application in new as well as existing Claus plants, low investment and utility costs, and a continuous gas phase catalytic process without water condensation or waste streams. In the Superclaus process, the Claus reaction [$\text{SO}_2 + 2\text{H}_2\text{S} = 3/8\text{S}_8 + 2\text{H}_2\text{O}$], which limits sulphur conversion because it is in equilibrium, is replaced by the reaction of H₂S with O₂, which is thermodynamically complete.

The Superclaus [7,8] catalyst is designed to give complete and highly selective conversion of H₂S to elemental sulphur, low formation of SO₂, and low sensitivity to water concentrations in the process gas so it has no Claus reaction reactivity. The catalyst [9] consists of active metal oxides on a carrier. Its properties include the following: H₂S conversion to sulphur higher than 85%, not sensitive to excess air, not sensitive to high water concentrations, no Claus reaction, no CO/H₂ oxidation, no formation of COS/CS₂, and chemically and thermally stable with good mechanical strength and long effective life.

Two options for the Superclaus process are the Superclaus 99 and the Superclaus 99.5 processes. Superclaus 99 consists of a thermal stage followed by three or four catalytic reactor stages, much like the Claus process. The first two or three catalytic stages are loaded with the standard Claus catalyst while the final stage is loaded with the new selective oxidation catalyst. In the Superclaus 99.5 process, a hydrogenation stage (using a cobalt/molybdenum catalyst) between the last Claus reactor and the selective oxidation

Table 2
Middle scale processes (aqueous phase).

Active specie	Process	Licensor
Ferric ion	Locat [10,11] Sulferox [10,12] Sulfint [13]	ARI Merichem Shell – Dow IFP
Vanadate (V)	Stretford [14] Unisulf [15]	British gas corporation, Unocal
Quinone	Hyperion [16] Takahax [17]	Ultrasytems Engineers Tokyo gas company
Bacteria	Thiopaque [18] Bio-SR [19]	Shell NKK

reactor is added. Sulphur recovery in the Superclaus 99 process with 2 Claus stages is in the range of 98.9–99.4% and in the range of 99.3–99.6% with 3 Claus stages. Sulphur recovery in the Superclaus 99.5 process is in the range of 99.2–99.6% with 2 Claus stages and 99.4–99.7% with 3 Claus stages.

2.2. Process for removal of H₂S

The processes for removal of intermediate quantities of H₂S (between 20 ton/day equivalent sulphur and 25 kg) can be divided into two main groups: the processes in aqueous phase and the processes which use either an organic solvent or no solvent at all.

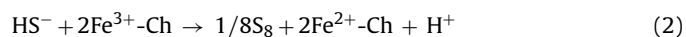
2.2.1. Aqueous phase processes (intermediate quantities)

The aqueous phase processes are based on solutions of oxidant species which are reduced by H₂S, which is therefore oxidised to sulphur. Re-oxidation of reduced specie is performed with air under mild conditions.

The oxidant species may be inorganic such as ferric, vanadate (V), quinone ions or bacteria (Table 2).

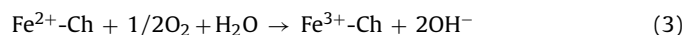
Locat [10,12] is the most widely used with more than 120 plants worldwide, followed by Sulferox with 20 plants.

These processes are based on an alkaline ferric solution in which hydrogen sulphide is adsorbed and reacts with ferric ions, being oxidised to sulphur, reducing them to ferrous ion according to:

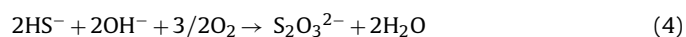


where Ch is a chelant, usually EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid) or analogous compounds.

In the following step, after sulphur separation, ferrous solution are re-oxidised by air according to:



Due to the high pH of the solutions some side reactions may occur, which consume the OH[−] ions such as: thiosulphate formation:



or carbonatation:

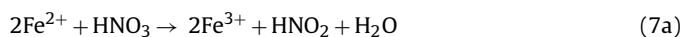
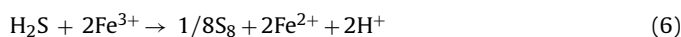


Sulphur produced by liquid phase processes, such as by Locat process, usually is not Claus grade, and cannot be commercialized as such. This is mainly due to the presence of chelants in solution, which are necessary to avoid iron sulphide precipitation due to high pH. The chelants are oxidised by air during solution regeneration, therefore sulphur produced by Locat and analogous processes is often contaminated by organic compounds. It may be also contaminated by traces of iron sulphide, which may be produced lowering chelants concentration.

It should be useful to perform reaction at low pH avoiding both the use of chelants, which are also quite expensive, and iron sulphide precipitation, but this is not possible because ferrous solutions are oxidised to ferric solutions extremely slowly at low pH. Recently Eni has presented a new process, at the moment at pilot plant scale, in which strong acid solutions of ferric nitrate are used [20].

The use of strong acid solutions avoid chelants and therefore the sulphur produced is of high quality (Claus grade). In this new process reduced ferrous ion solution is re-oxidised with a co-catalyst (Keggin heteropolyacid H₆PW₉V₃O₄₀).

The reaction scheme of Eni process is:



(probably both catalysed by H₆PW₉V₃O₄₀)

Unwanted side reaction is nitrous acid thermal decomposition with NO_x evolution according to:



This side reaction could be avoided by simply increasing oxygen partial pressure during ferrous solution re-oxidations [21].

2.2.2. Non aqueous phase processes

Non aqueous phase processes can be divided mostly into four classes:

- (1) “Chemical redox processes” in which the oxidation of H₂S to sulphur is performed using SO₂ as oxidant, dissolved in a solvent (Crystasulf [22], UCSR [23]).
- (2) “Cyclic redox process” in which H₂S is removed by oxidising it to sulphur with a solid catalyst. The reduced solid catalyst is re-oxidised with air (Caltech [24]).
- (3) “Direct oxidation processes”, in which the H₂S present in NG is directly oxidised to sulphur, without any previous separation (Sulfatreat DO (direct oxidation) [25]).
- (4) “Short contact time oxidation” of H₂S in NG, to a mixture of water, sulphur and. H₂, together with the oxidation of methane to CO and H₂ (SPOC [26], ASRL [27]).

To the first class belong Crystasulf and UCSR. Crystasulf removes H₂S by absorbing it in an organic solvent, in which H₂S reacts with SO₂ and is transformed into sulphur. It can also work under pressure, and can easily treat Claus tail gasses and streams with high concentrations of CO₂. Sulphur produced by this process is high purity crystalline sulphur, which can be commercialized without limitations. A commercial unit of Crystasulf, located in northwest Germany, can process 1.6 BCFD (45,313 m³/day) of NG from the North Sea.

An analogous process was developed by the University of California (UCSR), using a different organic solvent, but no industrial application has been announced to date.

To the second group belongs the Caltech process, in which H₂S reacts in a fixed bed reactor filled with solid sulphate, which is reduced to sulphite. H₂S is converted to liquid sulphur, which is separated. Sulphite is easily re-oxidised to sulphate, treating it at mild temperature under air flow.

To the third group belongs Sulfatreat DO. In this process H₂S is directly oxidised to sulphur with air in a fixed bed reactor filled with catalyst. The sulphur, obtained as vapour, is condensed and solidified. This process is effective also in streams with high content of CO₂ or hydrocarbons, and can remove more than 80% of the mercaptans present in the gas. A pilot plant with Sulfatreat DO process is located in Texas and it is treating 0.8 MSCFD (22,652 m³/day).

Table 3
Processes for mercaptans removal (high quantities).

Feedstock	Maximum content of mercaptans in the feed (as ppm sulphur)	Merox processes	Merichem processes	Sulphur content in the fuel after treatment
Natural gas, refinery gasses and LPG (liquefied petroleum gasses)	10,000	Merox extraction	Merichem extraction	Reduced
Light and medium naphtha, gasoline	5000	Liquid–liquid sweetening, fixed bed sweetening, Minalk sweetening	Liquid–liquid sweetening	Unchanged
Full boiling range naphtha, kerosene, jet fuel, diesel, heating oils	1000	Fixed bed sweetening, caustic free sweetening	Fixed bed sweetening	Unchanged

The last class is represented by SPCO (ConocoPhillips) and SCO (ASRL) processes. In both of them a stream of natural gas is treated at high temperature (from 700 up to 1500 °C), for a very short contact time (lower than 200 ms), in the presence of a catalyst, obtaining directly H₂S conversion to sulphur and water. The drawback of both the processes is that H₂S conversion is far from being complete (60–80%), obtaining hydrogen with relevant quantities of unconverted H₂S.

3. Mercaptans removal

3.1. Introduction

Mercaptans, or more correctly thiols, are organic compounds in which the group SH is present. They are described by the general formula RSH, where R can be either an alkyl or an aromatic group. Mercaptans are commonly present both in natural gas and liquid fuels such as gasoline, kerosene, jet fuel, diesel and heating oils. They have to be removed mainly for three reasons:

- (a) they are acid compounds and therefore they can cause serious corrosion problems,
- (b) they have an offensive odour hence they have to be removed from the fuel before it can be burnt,
- (c) most of them are highly toxic

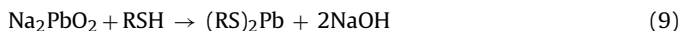
Mercaptans are present as low molecular (C¹–C⁴) and mostly straight chain compounds in gas and GPL, while in gasolines and middle distillates there are branched and heavier mercaptans.

3.2. Traditional removal methods

The treatment of fuels containing mercaptans has been investigated since 1860, and the traditional removal methods adopted are based on inorganic salts: “Doctor sweetening” [28] and “Copper sweetening” [29]. In these methods mercaptans are not removed from the fuel, but rather transformed into disulphides which are not corrosive and comparatively odourless. Hence after both of the

traditional treatments mentioned above the sulphur content in the fuel is not reduced by the treatment itself.

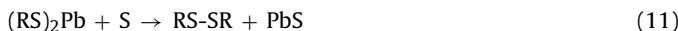
“Doctor sweetening”, which is the oldest one, is based on a lead salt: sodium plumbite (Na₂PbO₂). In the first step sodium plumbite solution, produced by dissolving lead oxide in sodium hydroxide solution, is shaken with the fuel which has to be treated. The two solutions do not mix together but the mercaptans in the oil react with sodium plumbite giving rise to the formation of lead mercaptide, which is soluble in the oil according to:



The lead mercaptide can be transformed again into sodium plumbite by reacting it with air according to:



The regeneration of sodium plumbite solution is very slow with this method and only partial. In order to obtain a complete conversion of lead mercaptide to disulphide, pure sulphur is added to the reaction mixture and lead mercaptide is completely converted to lead sulphide, which precipitates from the solution according to:



The conversion is complete, but lead sulphide cannot be regenerated and has to be disposed at the end of the reaction. Furthermore since sulphur, added to the reaction mixture to obtain disulphides, dissolves itself in the fuel, the sulphur content after the treatment increases. For these reasons this process is seldom applied today, except for analytical purpose.

The so-named “doctor test” is a common and ASTM listed method (ASTM D 4952-09) used to determinate the mercaptans content in a fuel and it consists of shaking a liquid fuel with a solution of sodium plumbite. A gasoline is “doctor sweet” (i.e. free of mercaptans), that is passes “doctor test”, when after been treated with a sodium plumbite solution, the addition of powdered sulphur fails to produce a precipitate of lead sulphide.

There is another traditional method for the conversion of mercaptans into nearly odourless and not acidic disulphides which is called “Copper sweetening”.

Table 4
Processes for small quantities of H₂S and mercaptans (solid phase).

Name of the process (Company)	Active phase	Kind of process	Regenerable	Maximum system capacity (lbs/day)	Specific features
Iron sponge (Connelly-GPM)	Iron oxide on wood shaving	Batch (slurry with water)	No	100	CO ₂ insensitive spent catalyst is pyrophoric
Sulfatreat [31] (Sulfatreat Company)	Hematite supported on porous material	Batch	No	200	CO ₂ insensitive
Sulphur-Rite (Merichem)	Iron oxide supported	Fixed bed	No	400	CO ₂ insensitive
Low temperature zinc oxide (ICI)	Zinc oxide	Fixed bed	No	300	Spent catalyst can be sold
Chemsweet (NATCO)	Zinc oxide + zinc acetate	Slurry of zinc salts in water	No	40	Spent catalyst can be disposed
Sulfosorb (Calgon carbon co.)	Active coal impregnate with copper salts	Fixed bed	Yes	3	Maximum content of sulphur in the feed 10 ppm.

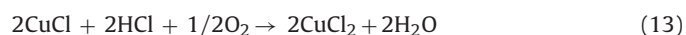
Table 5
Processes for small quantities of H₂S and mercaptans (aqueous phase).

Name of the process (Company)	Active phase	Kind of process	Regenerable	Maximum system capacity (lbs/day)	Specific features
Sulfa-check 2420 (Nalco-Exxon)	Aqueous alkali solution of NaNO ₂	Batch	No	200	Reacts also with CO ₂ lowest operative cost
Sulfascrub (Petroline Co.)	50% aqueous solution of triazine	Batch	No	100	Spent catalyst present disposal problems
The Eliminator (Merichem)	Solution of triazine	Batch	No	200	Spent catalyst present disposal problems

In this process copper is used as chloride, in the first step mercaptans are oxidised to disulphides according to:



The suspension of cuprous chloride is then oxidised again to cupric chloride with air according to:



Although these processes are still employed in some areas, the technologies described in the following sections are generally strongly preferred from the point of view of performance and costs.

3.3. Treatments of feed with high levels of mercaptans

There are mainly two kinds of process for the removal of relevant quantities of mercaptans in hydrocarbon streams: extraction, in which light mercaptans are oxidised to disulphides and removed, and sweetening, in which heavier mercaptans are oxidised to disulphides but are not removed from the stream. These methods are applied to remove large quantities of mercaptans from the hydrocarbons, from 200 kg per day of equivalent sulphur up to 30 ton and more of equivalent sulphur. For streams containing less than 200 kg per day of equivalent sulphur other methods are applied (scrubbing methods).

There are two main companies which are licensing processes for removal of big quantities of mercaptans: UOP (Merox processes [30]) and GTP-Merichem (Merichem processes) [31].

For each company different process configurations are used according to the nature of the feed to be purified, as shown in Table 3.

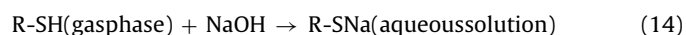
For a convenient application of every Merox or Merichem process a caustic pre-wash with dilute sodium hydroxide solution must take place before each treatment in order to remove all H₂S in the feed, whose content should not exceed 10 ppm., otherwise hydrogen sulphide reacts irreversibly with the strong alkalis solution used for the Merox (or Merichem) process.

Merox processes outnumber with a capacity installed and under construction exceeding 13 MMbpd (million barrels per stream day). Almost 1600 units have been commissioned as of January 2002, with capacity between 40 and 140,000 bpsd.

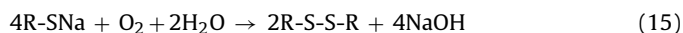
In the treatment of heavier feedstock, such as full boiling range naphtha, kerosene, jet fuel, diesel fuel, heating oils, the caustic pre-wash is needed also for the removal of naphthenic acids.

3.3.1. Extraction treatments

For the treatments of light feed stocks, such as natural gasses, refinery gasses, well gasses and LPG, in which low molecular weight mercaptans (from methyl mercaptan to butyl mercaptans) are present extraction processes are used. In the first step the gaseous stream reacts with a concentrated solution of sodium hydroxide (14 wt% NaOH) in which mercaptans are dissolved as the corresponding sodium salts according to:



The first step takes place in an extraction column, where mercaptans are washed by a counter current of caustic stream and the treated gas passes overhead. The aqueous solution containing mercaptans as sodium salts and the Merox or Merichem catalyst (a phthalocyanine complex of cobalt) flows from the bottom of the extraction column and is then heated and sent to an oxidiser. In the oxidiser the caustic solution reacts with air resulting in the oxidation of the mercaptides to disulphides according to:



The disulphides form a new oily phase, lighter than water and the two-phase mixture is sent to a separator. The regenerated caustic solution is sent to the extraction column while the oily phase is sent to appropriate disposal, e.g. injected into the charge of a hydro treating unit or, when possible, sold as a chemical specialty.

Using an extraction method a small amount of catalyst is periodically added to maintain sufficient process efficiency.

It is evident that with extraction treatments not only are the mercaptans transformed in not inoffensive lower toxic and non corrosive disulphide, but the sulphur content in the gas is also reduced since the disulphides produced from the oxidation of the mercaptans are removed.

The direct operating costs are estimated of 1.5 cent/10⁶ scf for the gas extraction and 0.4 cent/bbl for LPG extraction.

4. Treatments of feed with small quantities of H₂S and mercaptans

These “scrubbing treatments” are used when the content of mercaptans and hydrogen sulphide is low [32] (generally lower than 200 ppm calculated as total sulphur). Therefore the conventional treatments with amines (MEA, DEA, and MDEA) are not economically feasible. These processes are designed to be used for dilute streams, where the daily production of sulphur compounds does not exceed 400 lbs sulphur/day.

Most of the processes are stoichiometric reactions between sulphur containing molecules and the reactant, which cannot be regenerated and must be discharged and disposed. In Tables 4 and 5 are illustrated the most commonly used processes for the removal of low quantities of sulphur compounds.

5. Conclusions

Proper choice of treatment for natural gas containing H₂S and mercaptans depends on the quantity of these compounds both as concentration and as amount of equivalent sulphur.

For large quantities of H₂S the only process is Claus, with its different configurations and tail gas treatment processes, for intermediate (lower than 20 ton equivalent sulphur/day but higher than 25 kg) middle scale processes can be run both in aqueous phase and in organic or solid phase.

For large quantities of mercaptans (higher than 200 kg equivalent sulphur/day) the best processes for their removal from natural gas are extraction processes: Merox and Merichem ones.

For small quantities of H₂S and mercaptans the most economic choice is the use of scavengers, which can be divided according to their active phase, temperature of use, and regenerability.

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